CATALYTIC PYROLYSIS OF CASTOR SEED INTO LIQUID HYDROCARBON TRANSPORTATION FUELS

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Submitted By

RAHUL SAKHARE
109CH0099

Under the guidance

of

Prof. (Dr.) R.K.SINGH

Department of Chemical Engineering
National Institute of Technology
Rourkela

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CERTIFICATE

This is to certify that the work in this thesis entitled **"Catalytic pyrolysis of castor seed into liquid hydrocarbon transportation fuels"** submitted by **Rahul Sakhare (109CH0099)** in partial fulfillment of the requirements of the prescribed curriculum for Bachelor of Technology in Chemical Engineering Session 2009-2013 in the department of Chemical Engineering, National Institute of Technology Rourkela, Rourkela is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge the matter embodied in the thesis is his bona fide work.

Date :

Prof. R. K. Singh
Department of Chemical Engineering
National Institute of Technology
Rourkela - 769008

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Nomenclature

IEA	International Energy Agency
EIA	Energy Information Administration
GW	Gigawatt
ZSM	Zeolite Socony Mobil
MCM	Mobil Composition of Matter
XRD	X-ray Diffraction
FTIR	Fourier transform infrared spectroscopy
GC-MS	Gas chromatography–mass spectrometry
PID	proportional-integral-derivative
ASTM	American Society for Testing and Materials
BET	Brunauer–Emmett–Teller
SEM	scanning electron microscope

Abstract

Energy is essential for development and the demand for energy is increasing continuously due to the rapid outgrowth of population and urbanization. Biomass is found to be the maost promising source of many renewable enrgy sources. Pyrolysis is one of the most recent renewable energy processes, has been introduced and offers the advantages of a liquid product – bio-oil – that can be readily stored and transported, and used as a fuel, an energy carrier and a source of chemicals. Catalyst can increase the yield and quality of liquid product oil. In this paper, catalytic pyrolysis of castor seed was performed at 400^{o}C for different ratio of catalyst to biomass using zeolite catalyst. It was found that max yield of liquid was obtained at 1:5 ratio. Overall maximum yield of 62.73% was obtained in case of zeolite at the ratio of 1:5. As compared to the yield of thermal pyrolysis of castor seed without catalyst which was 64.4%, the yield of oil was significantly reduced after catalysis for the catalyzed reaction. It was also observed that the bio-oil contains compounds with carbon chain length in the range of C_4–C_{24} which is similar to most of fuels used.

1. INTRODUCTION

1.1. Trends in Energy Resources:

In this era of 21st century, modern people's life has become ecstasy due to science led massive industrialization and urbanization. It is well known fact that the main force behind modern man's progress is 'ENERGY'. All sector of society like economies, labor, environment, international relations in addition to our personal lives like food, health, housing, transportation, and more are pervaded by energy. People once had to depend on their own muscles to provide the necessary energy to do work. We have been relieved of much drudgery due to use of energy. It had also made our efforts more productive. Today muscles supply less than 1% of the work done in the industrialized world. Energy supplies play key role and acts as limiting factor to economic growth. World has become very interdependent and center for economic growth lies in access to reliable and adequate energy resources.

Pre-industrial society lived only on renewable forms of energy; that is, those sources that can be renewed or regenerated, such as water, wind, solar, and biomass. A shift to nonrenewable resources began in the eighteenth century, as an increasingly industrialized society started to burn fossil fuels to make steam for steam engines (invented in 1763) and to smelt iron. Currently, fossil-based energy resources, mainly coal, petroleum, and natural gas, are responsible for more than three quarters of the world's primary energy consumption, each corresponding to 36, 20, and 26%, respectively. Alternatives to fossil-based energy resources are nuclear power (8%) and renewable energy (9%), representing currently less than one quarter of the world's primary energy consumption [1]. Fig1. Shows the share of fossil fuels and renewable energy sources in world energy consumption in 2011 and 2040.

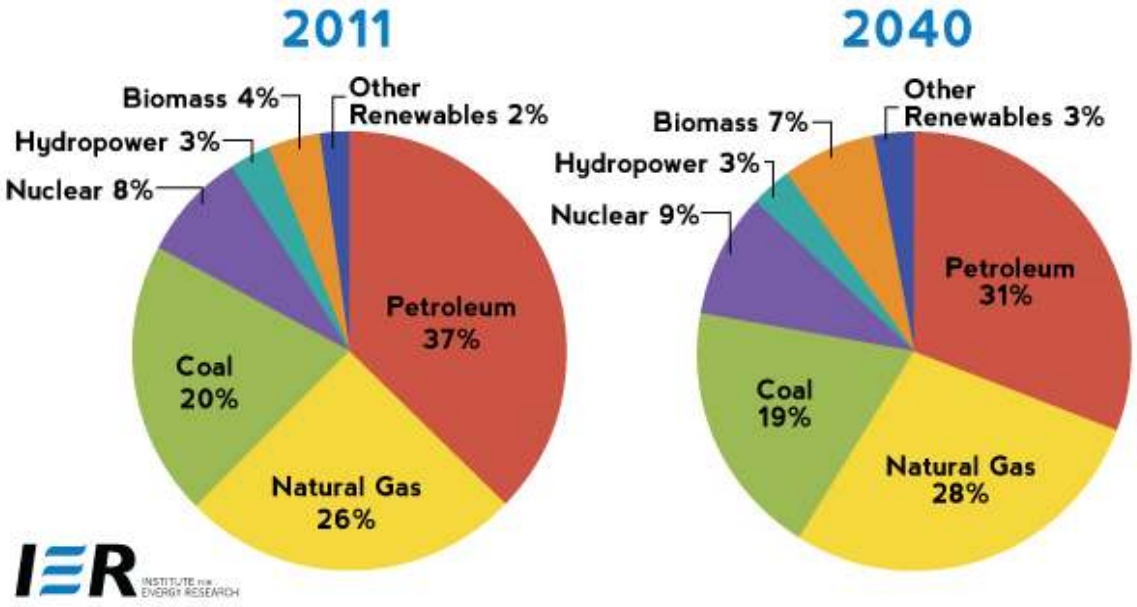

Fig.1. Energy Consumption Fuel Shares, 2011 and 2040[1]

Firstly, the way we produce and use energy today is not sustainable. Our main fossil fuel sources – oil, coal and gas – are finite natural resources which are getting depleted at a rapid rate. Our energy demands continue to increase while availability of conventional, cheap oil and gas are declining. According to the IEA, production from known oil and gas reserves will fall by around 40-60 per cent by 2030. It is clear that our dependence on fossil fuels cannot continue indefinitely. [1]

Secondly, processing and using unconventional fossil sources leads to production of large quantities of chemical pollution and greenhouse gases with severe impacts on biodiversity and ecosystem services. Now, Understanding energy use means also understanding the environmental result of its use. Even if we take into account fossil fuel supplies as infinite, there lies another compelling reason for an urgent switch to renewable energy which is 'Climate Change'. A major concern in the burning of fossil fuels is the possibility of large global climatic changes caused by increased levels of carbon dioxide and other greenhouse gases in the upper atmosphere. Severe health problems around the world have arisen due to effects of increased emissions of sulfur oxides, nitrogen oxides, and hydrocarbons. Acid rain caused by the emissions of coal-fired power plants harms trees, crops, and animals. The fragile balance of our planet's

ecosystems is endangered by global warming, and could abandon a quarter of all species to extinction. Conditions like extreme weather events, water shortages, crop failures, flooding already affect hundreds of millions of people worldwide which are likely to get worsened by increasing concentrations of greenhouse gasses in the Earth's atmosphere.

Nuclear power seems to be a part of the solution to the energy crisis because large-scale electricity is produced with low carbon emissions although mining and enriching uranium happens to be very energy intensive. But the major disadvantage associated to nuclear energy is that nuclear fission produces dangerous radioactive waste that remains highly toxic for thousands of years and it cannot be stored safely anywhere in the world. Moreover, materials and technology needed for nuclear energy can also be used to produce nuclear weapons which is very dangerous course to take in politically unstable world. Also nuclear technology requires a highly sophisticated and trained staff.

Thus, human society has come to stage where for the coming new century reconsideration and elucidation of new strategies has become necessary after two centuries of technical and economic progress. Renewable energy supplies are much more compatible with sustainable development than are fossil and nuclear fuels, in regard to both resource limitations and environmental impacts. Renewable energy will also help us develop energy independence and security. Actually, switching to renewable energy is one of the best choices considering future energy demands and environmental concerns. Therefore taking into consideration the finite nature of fossil and nuclear fuel materials, the harm of emissions and ecological sustainability, it is essential to expand renewable energy supplies and to use energy more efficiently.

Renewable energy technologies gained lot of importance three decades ago in response to the oil crisis of the 1970s, but the interest and support did not continue. In recent years, however, considerable improvements in the performance and affordability of solar cells, wind turbines and biofuels like ethanol and other fuels derived from plants—have boosted the way for mass commercialization. Renewable energy uses energy sources that are continually replenished by nature through various agents like the sun, the wind, water, the Earth's heat, and plants. It consists of various energy sources such as biomass, wind, solar, hydropower, geothermal, etc.

Among all these sources, biomass is one of the most common and widespread resources in the world.

1.2. Biomass

Bio-energy is the energy from biomass which all organic material originating from plants, trees and crops and is necessarily the collection and storage of the sun's energy through photosynthesis. Also, biomass for bioenergy comes either directly from the land, as energy crops, or from residues generated in the processing of crops for food or other products such as pulp and paper from the wood industry. Biomass was the first energy source utilized by humans and from early of all human history, wood has been our dominant energy source. Biomass is usually considered traditional energy source due to the role it plays, and continues to play, in most developing countries where it still accounts for an estimated one third of primary energy use while in the poorest up to 90% of all energy is supplied by biomass.Fig 2. Shows the of biomass energy in Renewable sources in total World energy consumption

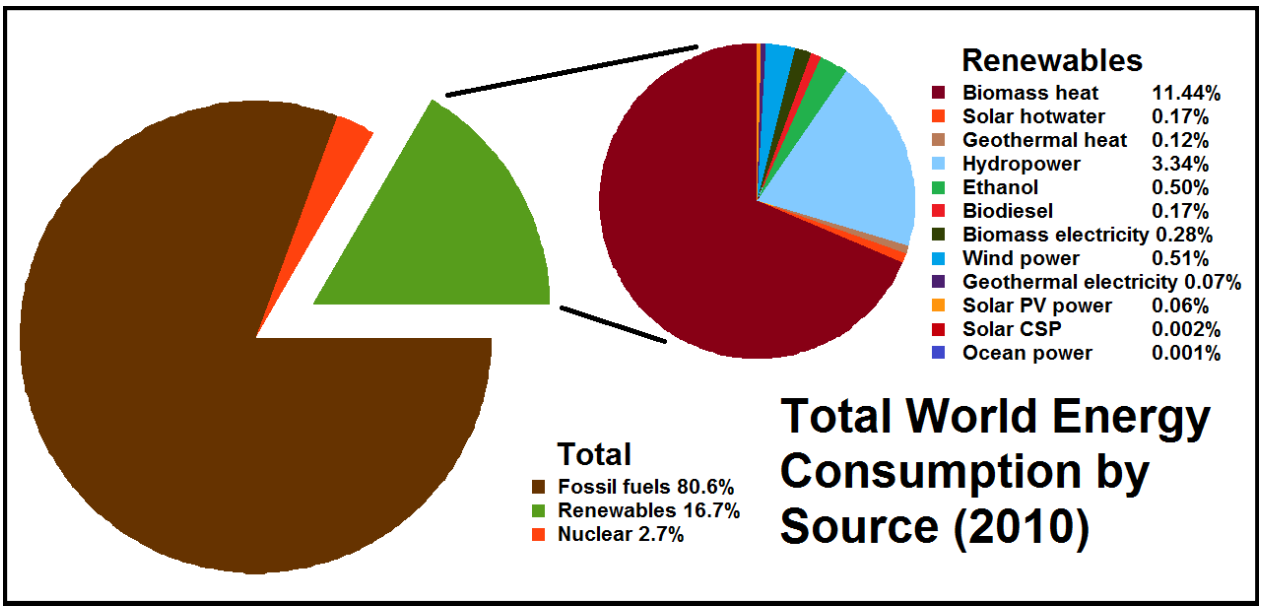

Fig 2. Total share of bio energy in Renewable sources of energy.[1]

Not all biomass is directly used to produce energy but rather it can be converted into intermediate energy carriers called biofuels. This includes charcoal (higher energy density solid fuel), ethanol (liquid fuel), or producer-gas (from gasification of biomass). Bioenergy is based on

resources that can be utilized on a sustainable basis all around the globe and can provide an effective option for the provision of energy services from a technical perspective.

Biomass energy is projected to play a major role in the future global energy supply. This is being driven by the recognized threat of global climate change which is caused largely by the burning of fossil fuels. Its carbon neutrality (when produced sustainably) and its relatively even geographical distribution coupled with the expected growth in energy demand in developing countries, where affordable alternatives are not frequently available, turn it to be a promising energy source in many regions of the world for the 21st century. Biomass energy has the potential to be "modernized" worldwide which means it can be produced and converted efficiently and cost-competitively into more convenient forms such as gases, liquids, or electricity. A variety of technologies can convert solid biomass into convenient, clean energy carriers over a range of scales from household/village to large industrial. Some of these technologies are commercially available today while others are still in the development stages. If widely employed, such technologies could enable biomass energy to play a much more significant role in the future than what is done today, especially in developing countries.

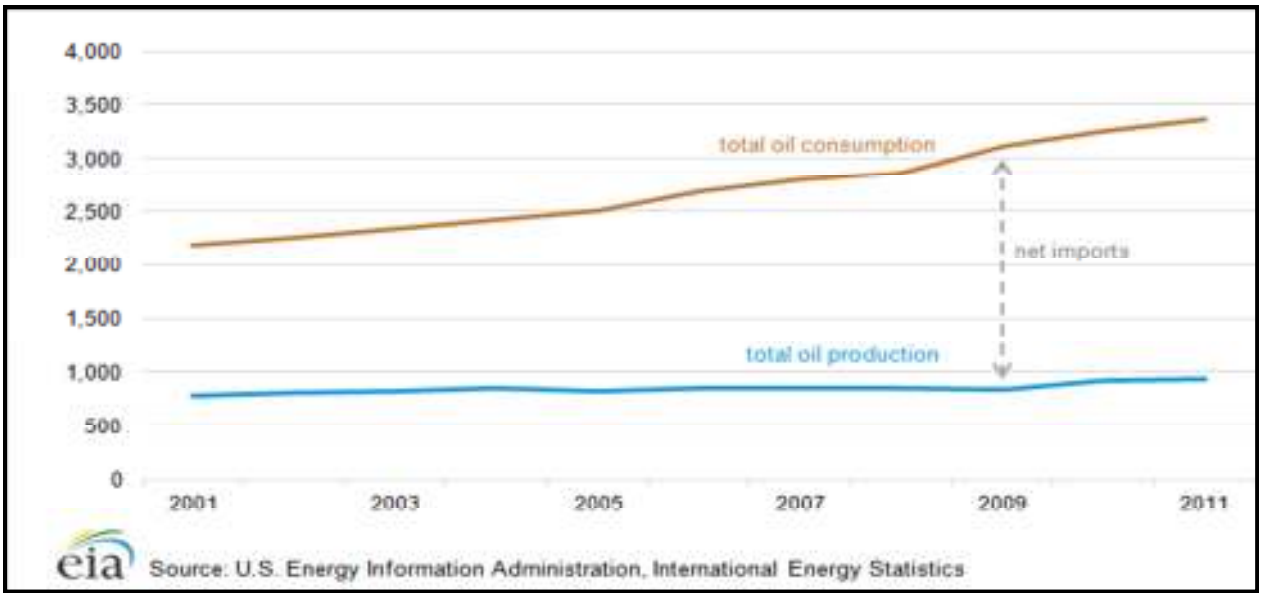

Fig. 3. India oil production and consumption

India's commercial energy consumption has been growing fast in recent years keeping pace with high economic growth rate.India is the fourth largest energy consumer in the world after the

United States, China, and Russia. India depends heavily on coal and oil for meeting its energy demand. It depends heavily on imports from other countries to meet this demand. Fig 3. shows the huge gap between energy production and consumption. Also this is the biggest source of national greenhouse gas emissions and pollution. So its use needs to be curtailed for reducing emissions of both greenhouse gases and local air pollutants. Renewable energy sources and technologies have potential to provide solutions to the long-standing energy problems being faced by the developing countries like India.[6]

In India, Biomass has always been an important energy source for the country. About 32% of the total primary energy use in the country is still derived from biomass and more than 70% of the country's population depends upon it for its energy needs [2]. Of all the renewable energy sources available in India, biomass (ligneous, herbaceous crops, agricultural and municipal wastes) is the largest, most diverse and most readily exploitable resource [3]. Large parts of India rely on biomass as the primary cooking fuel. According to the 2011 India census, 62.5 percent of households in rural areas use firewood as the primary cooking fuel, 12.3 percent use residue of crop as the primary cooking fuel, and 10.9 percent use dung. Biomass is also used in power sector in India. According to the Ministry of New and Renewable Energy, there are 288 biomass power and cogeneration plants in India with 2.7 GW of installed capacity and possess potential biomass electricity generation capacity of 18 GW. Biomass used for electricity generation largely comes from bagasse (crushed sugarcane or sorghum stalks), which has potential to be used in combustion-powered generators [4]. Also, biofuels in India are in large interest as a substitute to petroleum-based fuels, with a intention of enhancing energy security and promoting rural development. An ambitious target of substituting 20% of fossil fuel consumption by biodiesel and bioethanol by 2017 has been announced by India. India has announced a national biofuel policy and launched a large program to promote biofuel production, particularly on wastelands. [5]

1.3. Biomass Conversion Technologies:

Biomass can be converted into useful forms of energy using a number of different processes. One of the main factors which influence the choice of conversion process is the desired form of

the energy. Based on this, biomass can be converted into three main products transportation fuels, power/heat generation and as a chemical feedstock. The first two are related to energy conversion.

Now, conversion of biomass to energy is carried using two main process technologies.

1. Thermo-chemical
2. Bio-chemical

1.3.1. Themochemical Conversion Process

In thermo-chemical conversion, four process options are available:

1. Combustion,
2. Pyrolysis,
3. Gasification and
4. Liquefaction.

The method which was found to be suitable and is used is the pyrolysis of the biomass.

1.3.2. Pyrolysis

Pyrolysis of biomass can be described as the direct thermal decomposition of the organic matrix in the absence of oxygen to obtain an array of solid products (char and charcoal), liquid products (wood tar, tar, oil, and pyrolytic oil) and gas products (wood gas and pyrolytic gas). Commercial production of a wide range of fuels, chemicals, solvents and other products from biomass feedstocks has been done using pyrolysis method. Conventional pyrolysis consists of the slow, irreversible, thermal decomposition of the organic components in biomass. Slow pyrolysis has traditionally been used for the production of charcoal. Short residence time pyrolysis (fast, flash, rapid, ultra pyrolysis) of biomass at moderate temperatures has generally been used to obtain high yield of liquid products. Fast pyrolysis is characterized by high heating rates and rapid quenching of the liquid products to terminate the secondary conversion of the products [8]. Depending on the pyrolysis temperature, the char fraction contains inorganic materials ashed to varying degrees, any unconverted organic solid and carbonaceous residues produced from thermal decomposition of the organic components. The liquid fraction comprises of a complex mixture of water and organic chemicals like alcohols, esters, aldehydes, acids, ketones,

heterocyclic derivatives and phenolic compounds The pyrolysis gas mainly contains CO_2, CO, CH_4, H_2, C_2H_6, C_2H_4, minor amounts of higher gaseous organics and water vapour [9]. Problems with the conversion process and subsequent use of the oil, like its corrosivity and its poor thermal stability, still need to be overcome. Upgrading bio-oils by lowering the oxygen content and removing alkalis by means of hydrogenation and catalytic cracking of the oil may be required for certain applications.

1.3.3. Catalytic Pyrolysis

The pyrolysis oil is highly oxygenated, corrosive, viscous, chemically very complex and relatively unstable. The following properties need to be improved to make the oil suitable as a transportation fuel:

- Acidity needs to be reduced
- Energy density needs to be higher
- Lower viscosity
- Modified miscibility with fossil fuels
- Particulates upon heating or during storage is less

Catalytic pyrolysis is considered to be an emerging technology for bio-oil production. It is a promising technology for producing transportation fuels that are compatible with current petroleum products. Currently, catalytic pyrolysis of different biomasses have been greatly studied to increase bio-oil yield or improve its quality. There are many types of catalysts, such as molecular sieve, metal oxide, transition metals, mineral and so on. The undesirable properties of pyrolysis oil result from the chemical composition of bio-oil that mostly consists of different classes of oxygenated organic compounds. The elimination of oxygen is thus necessary to transform bio-oil into a liquid fuel that would be broadly accepted and economically attractive. Two types of processes that have been used to reject oxygen from organic molecules are hydro-treating and catalytic cracking. The former uses hydrogen to remove oxygen in the form of water while the latter accomplishes the removal of oxygen in the form of water and carbon oxides using shape-selective catalysts like zeolites. Since the bio-oil produced through pyrolysis is highly oxygenated, different catalysts can be used to upgrade its quality by deoxygenation reactions. In particular, the concentration of oxygenates in the oil can be reduced by using acidic

zeolite catalysts. Fuel properties can be improved by decreasing the amount of oxygen in the bio-oil, which can be achieved through deoxygenation over different acidic zeolites catalysts.

2.Literature Review:

Richard F., Stefan C. evaluated a set of commercial and laboratory-synthesized catalysts for their hydrocarbon production performance via the pyrolysis/catalytic cracking path. Three types of biomass feedstocks; cellulose, lignin, and wood were pyrolyzed. The highest yield of hydrocarbons (approximately 16 wt.%, including 3.5 wt.% of toluene) was achieved using nickel, cobalt, iron, and gallium-substituted ZSM-5[10]. N. Kumar carried out Catalytic pyrolysis of biomass from pine wood in a fluidized bed reactor at 450^0C using different zeolite catalyst. They found that, the structures slightly influenced the yield of the pyrolysis product phases, at the same time the chemical composition of the bio-oil was dependent on the structure of acidic zeolite catalysts[11]. Review of Catalytic Pyrolysis of Biomass for Bio-oil focuses on the recent developments in catalysts used in pyrolysis of biomass for bio-oil production. 5 types of catalysts such as mineral, metal oxide, transition metal, molecular sieve and others, were studied. Molecular sieves, such as HZSM-5, ZSM-5, MCM-41, SBA-15, HUSV, REV and their modified catalysts are most widely used in biomass catalytic pyrolysis process. Among the 5 types of catalysts mentioned, molecular sieves are the most popular one, which have also desired effect on bio-oil producing, such as higher yields, better stability and so on[12]. Esben Taarning and others reviewed and discussed the developments that have taken place in the field of biomass conversion using zeolites. Emphasis was put on the conversion of lignocellulosic material to fuels using conventional zeolites as well as conversion of sugars using Lewis acidic zeolites to produce useful chemicals. Zeolites can be used for the production of gasoline from methanol (gasification), ethanol (fermentation) and oxygenates (pyrolysis), thereby covering the most likely bio-refineries. Finally, zeolites could replace, or supplement, biochemical processes in some cases[13].

Pan Wang, Sihui Zhan investigated Pyrolysis of herb residue in a fixed-bed to determine the effects of pyrolysis temperature and catalysts (ZSM-5, Al-SBA-15 and alumina) on the the qualities and products yields of bio-oils. The results indicated that the maximum bio-oil yield of 34.26% was obtained at 450^0C with 10 wt.% alumina catalyst loaded. The order of the catalytic effect for upgrading the pyrolytic oil was Al_2O_3 > Al-SBA-15 > ZSM-5. The bio-oil with the highest calorific value (25.94 MJ/kg) and the lowest oxygen content (26.71%) was obtained with 20 wt.% alumina catalyst loaded. It was also found that the alumina catalyst could clearly enhance the formation of aliphatics and aromatics[14]. Ilknur Demiral, Sevgi S_ensoz et al.conducted pyrolysis of olive and hazelnut bagasse biomass samples with two selected

catalysts, namely sodium feldspar and activated alumina,in a fixed-bed reactor. The effects of catalysts and their ratio (10%, 20%, 30% and 40% w/w) on the pyrolysis product yields were investigated and the results were compared with the results of experiments performed without catalyst under the same conditions. Bio-oil yield was decreased when compared with non-catalytic experiments for both biomass samples and catalysts. However Activated alumina and sodium feldspar catalysts addition provided a higher calorific value to the bio-oil. All the bio-oils were characterized by low oxygen content with a high H/C ratio. Comparison of the H/C ratios with conventional fuels indicates that the H/C ratio of the bio-oils is very similar to that of light petroleum products[15]. Huiyan Zhang a, Rui Xiao a, He Huang b, Gang Xiao investigated Fast pyrolysis of corncob with and without catalyst in a fluidized bed to determine the effects of pyrolysis parameters (gas flow rate, temperature, particle size and static bed height) and a HZSM-5 zeolite catalyst on the qualities and product yields of the liquid products. They found out that the presence of the catalyst increased the yields of water and coke, non-condensable gas, while decreased the char and liquid yields. The elemental analysis showed that more than 25% decrease in oxygen content of the collected liquid in the second condenser with HZSM-5 was observed compared with that without catalyst[16]. Paul T. Williams, Nittaya Nugranad did comparison of products from the pyrolysis and catalytic pyrolysis of rice husks. Zeolite ZSM-5 catalyst was used for upgrading the pyrolysis vapors. The pyrolysis oils before catalysis were highly oxygenated, of low viscosity and homogeneous. In the presence of the catalyst the yield of oil was markedly reduced, although it reduced the oxygen content of the oil with the formation of coke on the catalyst. The impact of the catalyst was to convert the oxygen in the pyrolysis oil to largely CO and CO_2 at the higher catalyst temperatures and to largely H_2O at the lower catalyst temperatures. The catalysed oils were significantly increased in single ring and PAH compared to uncatalysed biomass pyrolysis oils. The molecular weight distribution of the oils was decreased after catalysis and further decreased with increasing temperature of catalysis. The concentration of aromatic and polycyclic aromatic species increased with increasing catalyst temperature[17].

Different types of MCM-41 materials as potential catalysts in the catalytic biomass pyrolysis process were evaluated. Three different samples of Al-MCM-41 materials (with different Si/Al ratio) and three metal containing mesoporous samples (Fe–Al-MCM-41, Cu–Al-MCM-41 and Zn–Al-MCM-41) have undergone synthesis, characterization and testing as catalysts in the

biomass catalytic pyrolysis process using a fixed bed pyrolysis combined with a fixed catalytic reactor and two different types of biomass feeds. All catalysts were found to increase the amount of phenolic compounds, which play very important role in the chemical (adhesives) industry. A low Si/Al ratio had a positive effect on product yields and composition. Cu–Al-MCM-41 and Fe–Al-MCM-41 are the best metal containing catalysts in terms of production of phenols. The presence of the Al MCM-41 material decreased the fraction of undesirable oxygenated compounds in the bio-oil produced, which indicates that the bio-oil produced is more stable [18]. Pyrolysis of biomass was carried out in a fluidized bed unit (5 kg/h) with the objective of maximizing yield of liquid. Liquid product which was formed in pyrolysis was separated into two phases: water phase and oil phase. The oil phase was improved by sulfided Co–Mo–P catalyst in an autoclave. It was found out that the significant difference between the raw pyrolytic oil and the upgraded oil was that the former was methanol-soluble while the latter was oil-soluble [19].

Hybrid catalysts consisting of a zeolite (ZSM-5 or Beta) and bentonite as a binder were prepared and characterized by pyridine FTIR, XRD and nitrogen adsorption. The hybrid catalysts showed similar properties as the combined starting materials. Catalytic pyrolysis over Beta and pure ZSM-5 as well as hybrid catalysts has been successfully carried out in a dual-fluidized bed reactor. De-oxygenation of the bio-oil which was produced over the different zeolitic materials was increased compared to non-catalytic pyrolysis over quartz sand [20]. Biodiesel from Jatropha Curcas oil (JCO) with impregnated bentonite was studied. In this study, transesterification of Jatropha Curcas oil were investigated using Ba/Bentonite, Na/Bentonite, K/Bentonite as heterogeneous catalyst. The activity of catalyst with various reaction variables on yield of biodiesel was carried out in the presence of methanol. The characterization of impregnated bentonite and natural bentonite was conducted by X-ray Fluorescence and X-ray Diffraction analysis. The highest of methyl ester with Na/bentonite as catalyst was 84.84%wt.[21]

3.Materials and Methods

3.1. Materials

3.1.1. Raw material(biomass feed)

The raw material, castor seeds are directly used as feed to the reactor. Fig. 1 shows the photograph of castor seed, used as feed.

Fig. 4. Castor Seed

3.1.2. Catalyst:

Three catalyst were used namely Bentonite, Molecular sieve, Zeolite.

Bentonite:

Bentonite is an absorbent aluminium phyllosilicate, mostly impure clay consisting majorly of montmorillonite. Different types of bentonite are there, each named after the respective dominantelement, such as potassium (K), sodium (Na), calcium (Ca), and aluminium (Al). Bentonite used in the process was colloidal native hydrated aluminium silicate.

Molecular Sieve:

A molecular sieve is a material with very small holes of precise and uniform size which are small enough to block large molecules and allow small molecules to pass. The diameter of a molecular sieve is measured in Angstroms (Å) or nanometers (nm). Molecular sieve used in the experiment was of 13X category and is crystalline sodium aluminosilcate. Its specifications are pore size of

10 Å, bulk density of 0.55~0.65, Attrition Abrasion of 0.3~0.5. It is used in desiccation, desulphurization and purification of petroleum gas and natural gas.

Zeolite:

Zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents. They have a porous structure that can accommodate a wide variety of cations, such as Na^+, K^+, Ca^{2+}, Mg^{2+} and others. Some of the more common mineral zeolites are Some of the more common mineral zeolites are chabazite, analcime, heulandite, clinoptilolite, natrolite, phillipsite, and stilbite. There are four basic grades of molecular sieves. These grades differ from one another due to their chemical composition and pore size. The particle size of the zeolite used in

the experiment is < 10 micrometer.

Fig. 5. Different Catalyst used – (from left) Zeolite, Bentonite, Molecular Sieve

3.2. Experimental set up

The photo graph of the experimental set up is given in Fig. 6. The pyrolysis unit consists of PID controller, electrical heated furnace, pyrolysis reactor, glass condenser and measuring cylinder. The temperature of the furnace was maintained by highly sensitive PID controller. Water is circulated as cooling medium in the condenser via a pump. The reactor is cylindrical shaped vessel made up of stainless steel.

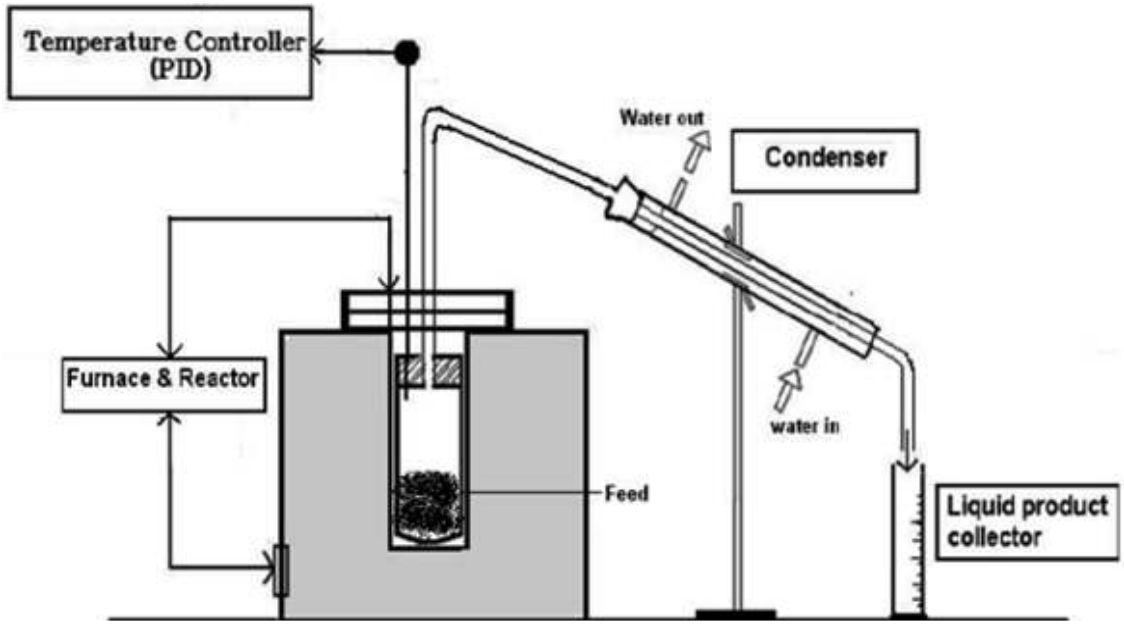

Fig. 6. Experimental Setup

3.3. Experimental Procedure:

The seed, raw materials were purchased from market and used directly as feed to the reactor. A series of experiments were conducted to determine the influence of different catalyst to biomass ratios between 1:3 to 1:6 at 550^{o}C at a rate of 20^{0}C/min. These series of experiments were conducted with previously mentioned three catalyst. The pyrolysis experiments were performed in a semi batch reactor, inserted vertically into an electrically heated furnace. The temperature is controlled by a PID controller. 15 gram of castor seeds as feed was pyrolyzed at each run and the vapors generated from the reactor was condensed in a condenser cooled by water. The condensed liquid was collected in a cylinder and separated into two fractions (aqueous and fuel) by technique called gravity separation as shown in fig.

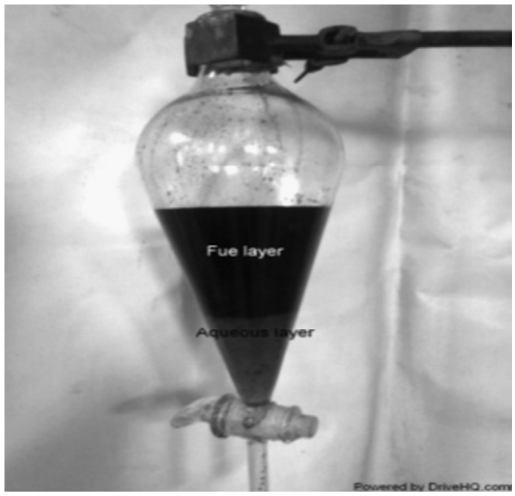

Fig. 7. Gravity separation of pyrolytic oil.

The residue (char) in the reactor is known as pyrolytic char. The residue or char was collected after cooling the reactor. During sample runs various data like yield of char, reaction time, and yield of liquid product were noted down. Variation in liquid product, yield of char, and gas (volatiles) with respect to temperature is plotted. Variation in reaction time with respect to temperature was also plotted.

3.4. Characterization of Raw Material and Char

The Castor seed and pyrolytic char were analyzed in order to observe the variation in the properties of the solid material because of pyrolysis.

3.4.1. Proximate Analysis:

It is simple means of determining the distribution of products obtained when the coal sample is heated under proper stipulated conditions. As defined by ASTM D 121, proximate analysis separates the products into four groups: (1) moisture, (2) volatile matter, comprising of vapors and gases driven off during pyrolysis, (3) fixed carbon which is the nonvolatile fraction of coal, and (4) ash, the inorganic residue remaining after combustion.

3.4.2. Ultimate Analysis

The Ultimate analysis was carried out using an CHNSO elemental analyser. It is otherwise known as elemental analysis which determines the carbon, hydrogen, nitrogen, sulphur and the oxygen content in the material. The oxygen component of the material is calculated by difference

after the calculation of carbon, hydrogen, nitrogen &sulphur content .The elemental analysis was done for bio-mass, bio-oil as well as the bio-char also.

3.4.3. Surface Area of Char

3.4.3.1. BET

Surface area of the char obtained was calculated, to investigate its utility as an adsorbent by using a Surface Area Analyzer.

3.4.3.2.SEM

SEM is used to determine the morphology of the material under view. Images are produced of a sample by scanning it with a focused beam of electrons. Atoms in the sample interact with the electrons, producing various signals that can be detected and which contain information about the sample's composition and surface topography. The electron beam is generally scanned in a raster scan pattern after which the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution which is better than 1 nanometre. The surface of the char obtained was viewed under a Scanning Electron Microscope (Model: JEOL-JSM-6480LV SEM) at different magnification values to have a clear view on pore density and size.

3.5. Chemical Characterization of Bio-Oil

3.5.1. FTIR

An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. In order to determine the functional groups present in the pyrolytic oil, Fourier Transform Infrared spectroscopy of the oil was analyzed in a Perkin-Elmer infrared spectrometer. The absorption of infrared radiation causes excitation of the atoms or molecules thereby causing to vibrational bands which is calculated as wave number cm^{-1}. The ominc software is used to correct the medium's background material used during analysis. Samples are dried prior to analysis and then were mixed with (1:200) (w/w) and then hydraulically pressed and then set for analysis.

3.5.2. GC-MS Analysis

Gas Chromatography – Mass Spectrometry of the pyrolytic oil was performed using a GC-MS OP 2010[SHIMADZU] analyzer in Sargam Laboratory, Chennai to determine the chemical compounds present in the oil. Gas chromatography–mass spectrometry (GC-MS) is a method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances within a test sample. In GC-MS analysis the mobile phase is the gas phase generally helium gas is being considered. During the analysis a column is being used the mixture of compounds in mobile phase interacts with the stationary phase and thereby causing the separation based on the rate of interaction which interacts first will analyzed and then the next.

4.Results and Discussions

4.1. Proximate and Ultimate analysis of Biomass

Table 1. Proximate and Ultimate Analysis of raw material[23]

PROXIMATE ANALYSIS	
Content	**Weight percentage (%)**
MOISTURE CONTENT	27.37
VOLATILE MATTER	61.29
FIXED CARBON	9.14
ASH CONTENT	2.2
ULTIMATE ANALYSIS	
Elements	**Weight percentage (%)**
CARBON	59.288
HYDROGEN	6.167
NITROGEN	2.45
SULPHUR	0.03
OXYGEN	30.095

The proximate and ultimate analysis of all raw materials are presented in Table 4.1 and Table 4.2 respectively which shows that the raw materials contains higher percentage of volatile matter and less amount of moisture and ash content and higher weight percentage of oxygen followed by carbon and hydrogen with a fewer amount of sulphur.

4.2. Influence of Catalyst to Biomass ratio on Yield %

Fig. 8., fig. 9 and fig. 10, shows the product yield at 550^0C for different catalyst to biomass ratio ranging from 1:6 to 1:2 for Catalytic pyrolysis of castor seed in case of bentonite, Molecular Sieve and Zeolite respectively. It was observed in all cases that the yield of liquid product

increases with increase in ratio. But up to a certain ratio which is different for different catalyst, the liquid increases and then decreases with increase in ratio. It was also observed that the oil yield increases with the decrease in char yield.

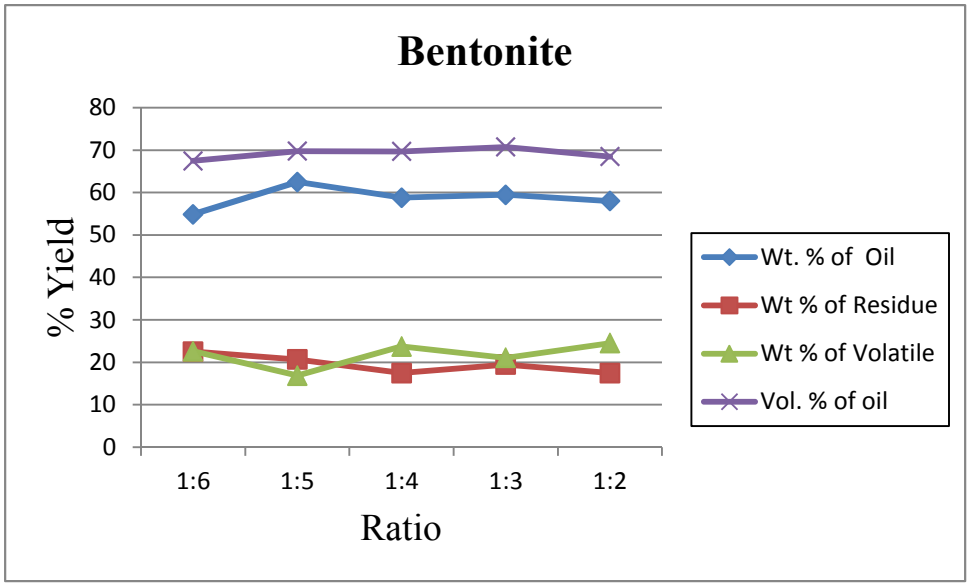

Fig. 8. Influence of Bentonite on catalytic pyrolysis of castor seed

Fig. 8. shows that max yield of 62.47% was obtained at the catalyst to biomass ratio of 1:5 in case of bentonite catalyst whereas char yield was minimum of 16.86%.

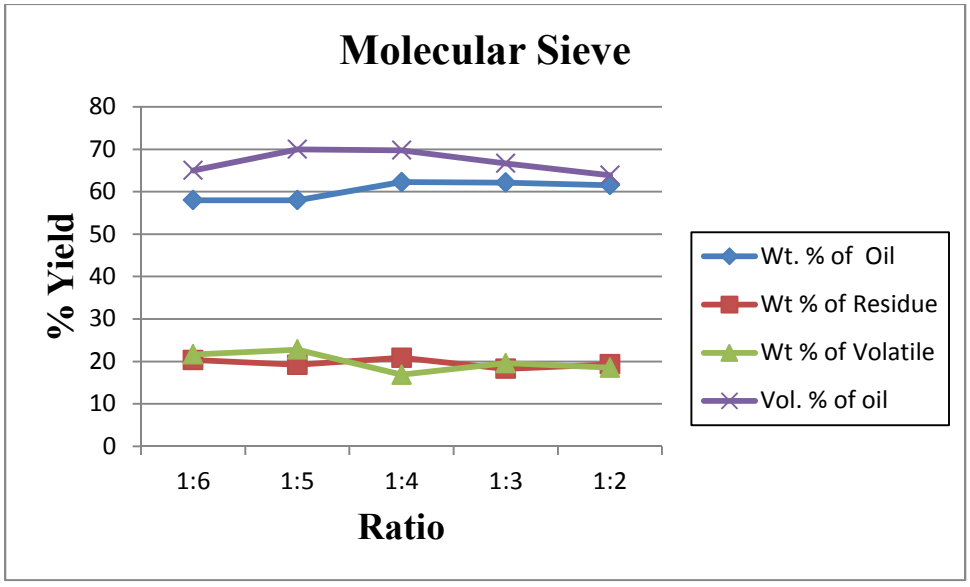

Fig. 9. Influence of Molecular Sieve on catalytic pyrolysis of castor seed

Fig. 9. shows that max yield of 62.27% was obtained at the catalyst to biomass ratio of 1:4 in case of bentonite catalyst whereas char yield was minimum of 16.86%.

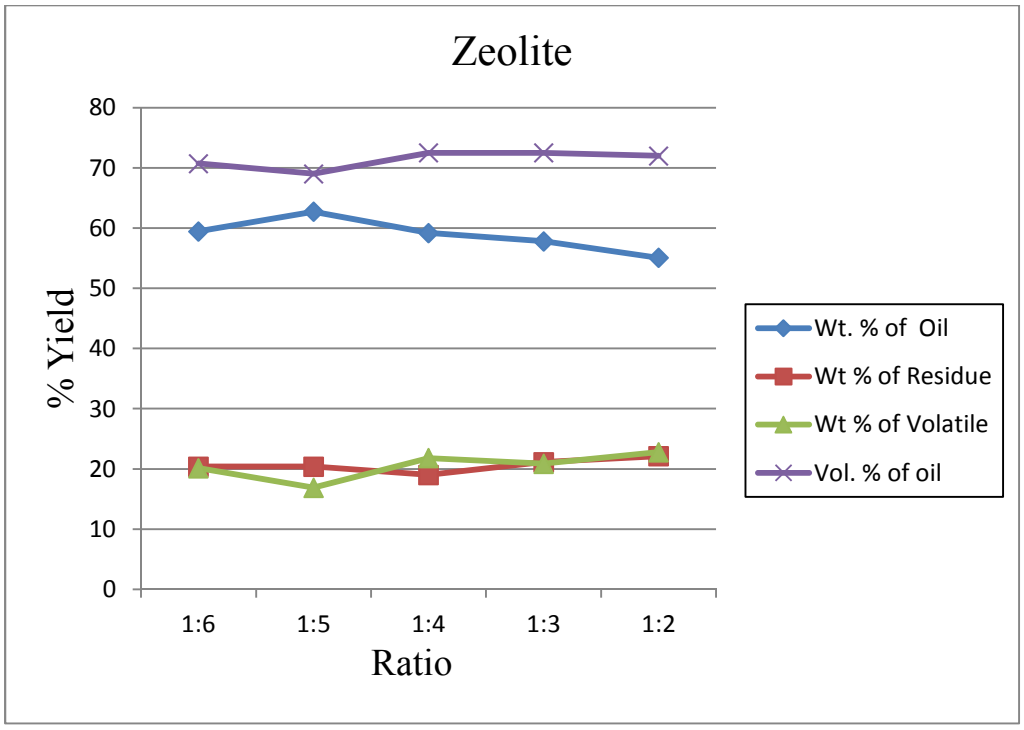

Fig. 10. Influence of Zeolite on catalytic pyrolysis of castor seed

Fig. 10. shows that max yield of 62.73% was obtained at the catalyst to biomass ratio of 1:5 in case of bentonite catalyst whereas char yield was minimum of 16.87%.

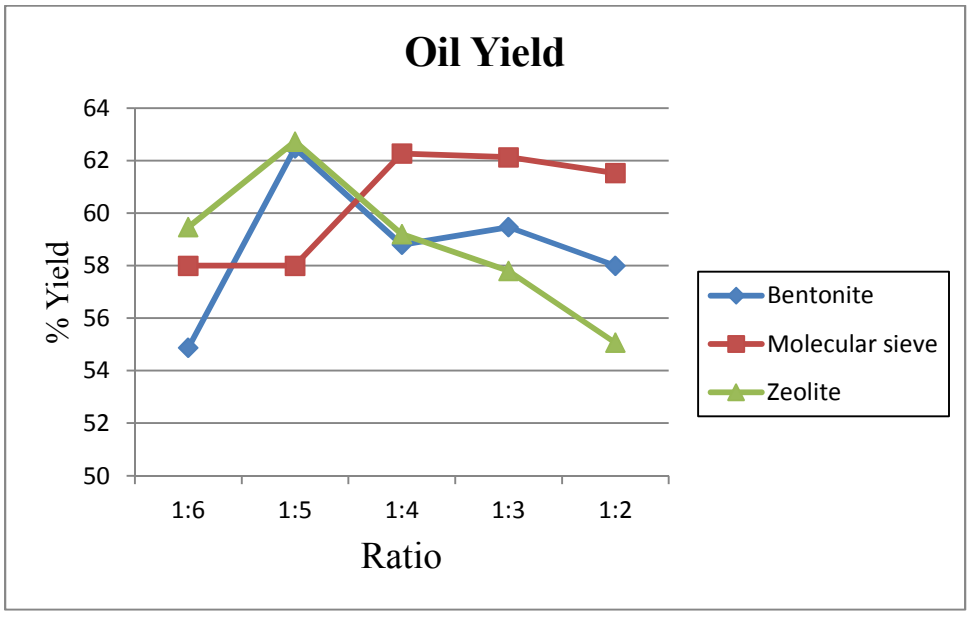

Fig. 11. Bio-oil yield of all three catalyst at different ratios

Fig. 11 shows that of all the three catalyst used in catalytic pyrolysis, treatment with zeolite gave the maximum oil yield of 62.73% with catalyst to biomass ratio of 1:5. As compared to the yield of thermal pyrolysis of castor seed without catalyst which was 64.4%, the yield of oil was significantly reduced after catalysis for the catalyzed reaction.

4.3. Effect of catalyst to biomass ratio on Completion time

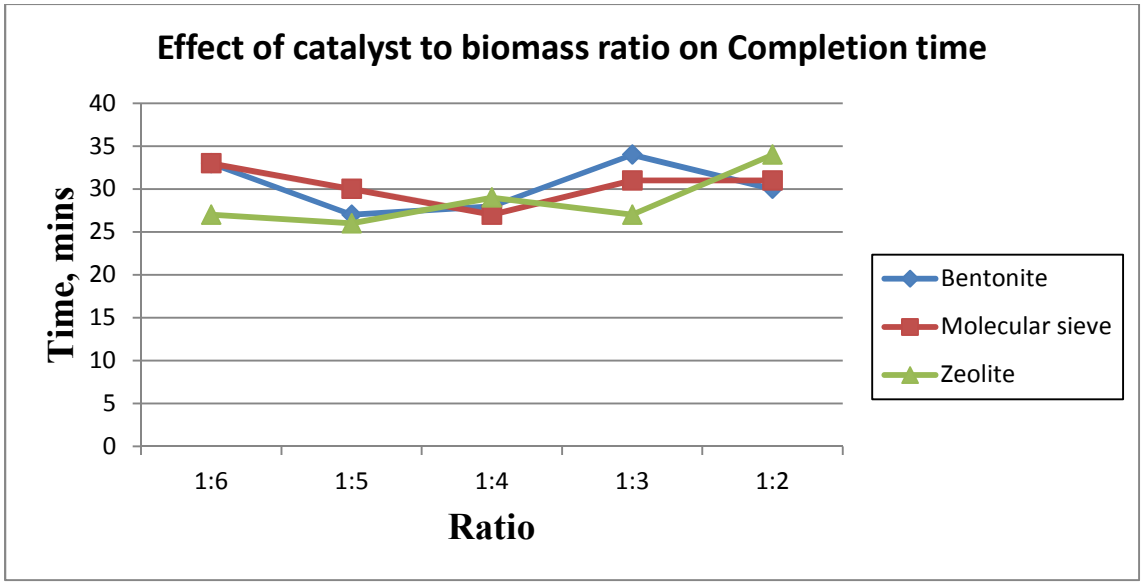

Fig. 12. Influence of Catalyst to biomass ratio on Completion time

Above fig. shows that reaction completion time was significantly reduced as compared to thermal pyrolysis. The minimum time was obtained with treatment of zeolite at the ratio of 1:5 which is found to be 26 mins.

4.4. FTIR analysis of pyrolytic oil

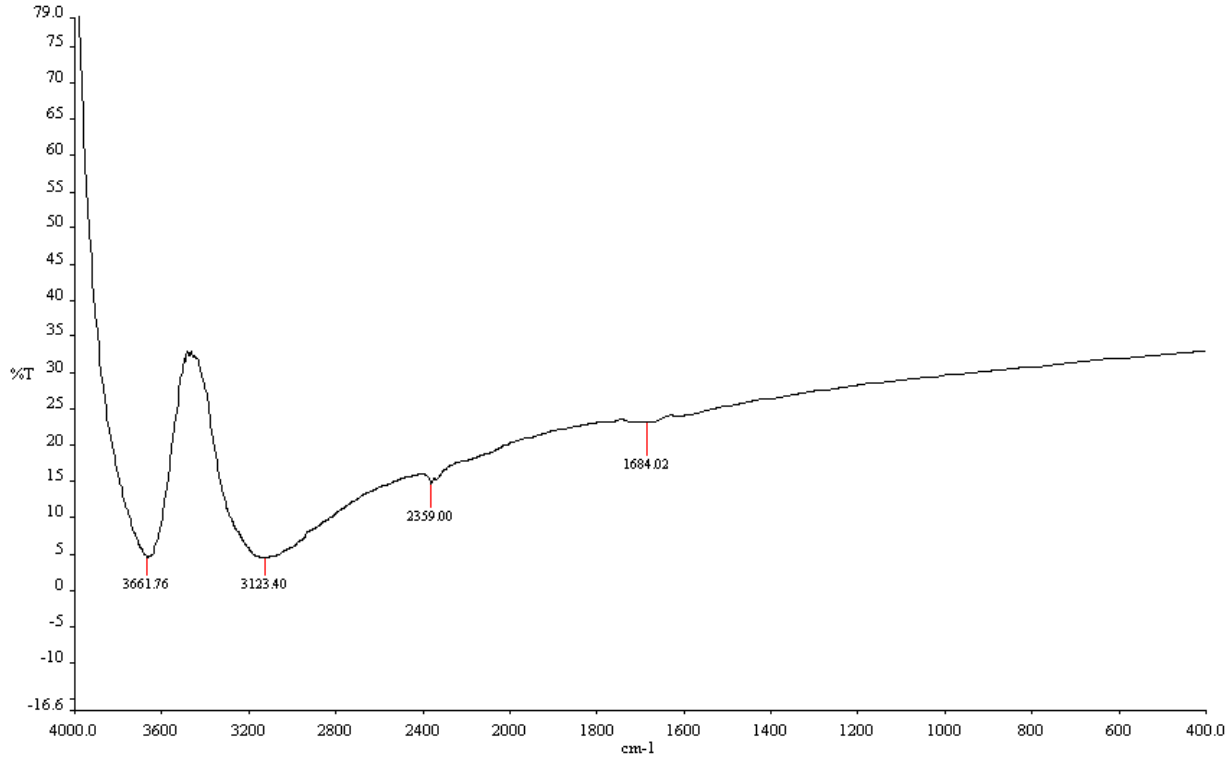

Fig. 13. FTIR spectra of bentonite treated pyrolytic oil

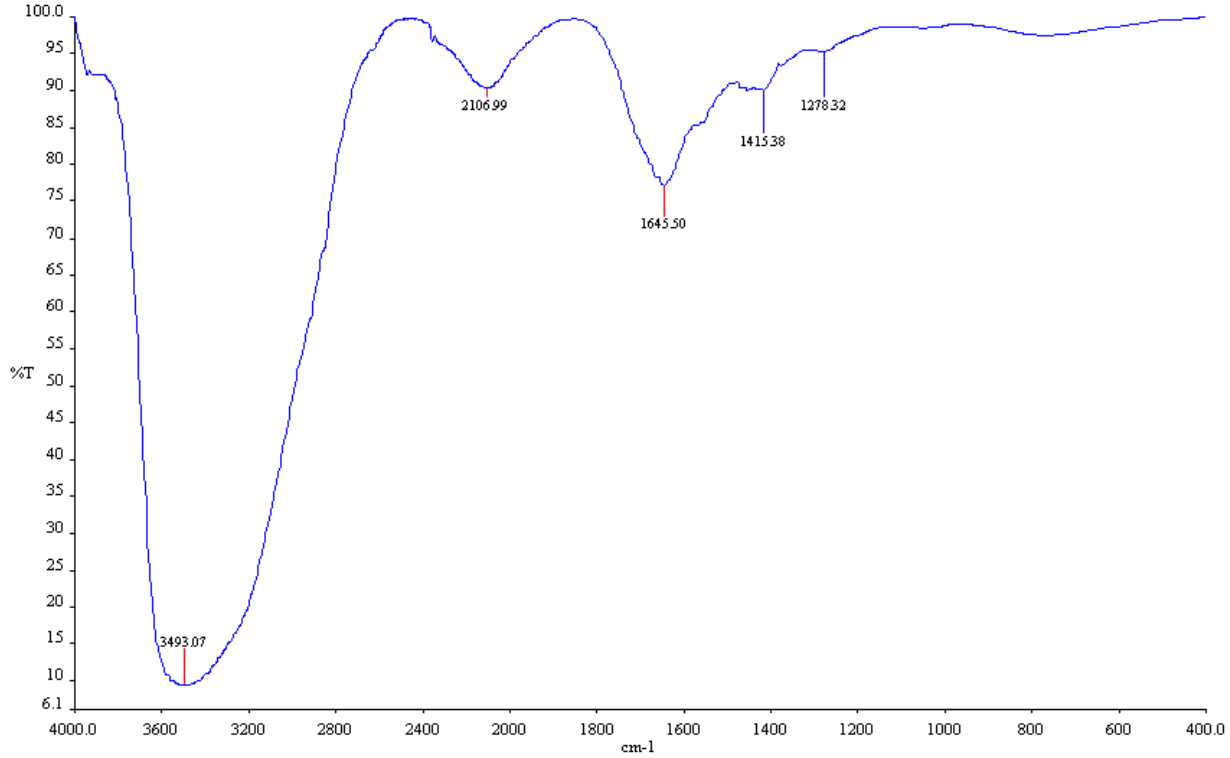

Fig. 14. FTIR spectra of Molecular Sieve treated pyrolytic oil

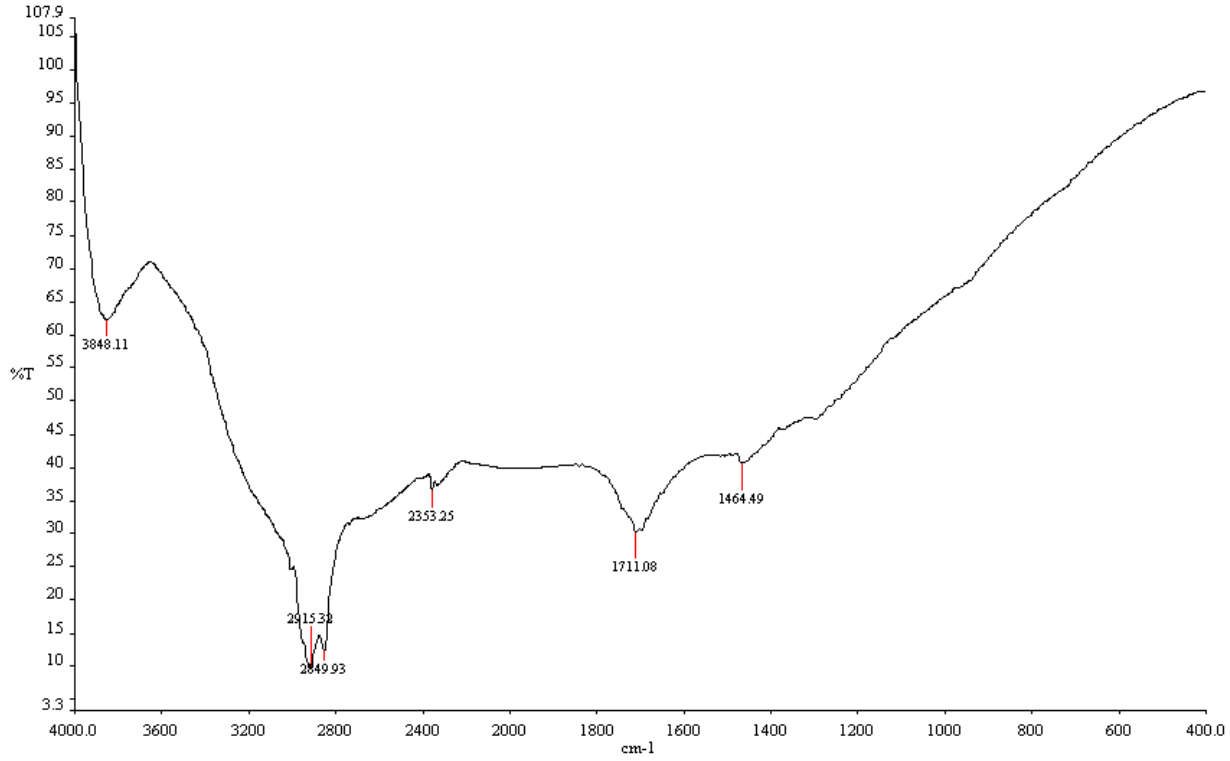

Fig. 15. FTIR spectra of Zeolite treated pyrolytic oil

Table 2. Functional groups presents in all pyrolytic oil

Frequency range(cm^{-1})	Groups	Class of compounds
3600-3300	O-H & N-H Stretching group	Low concentration alcohols, phenols, Primary Amine
3000-2840	C-H Stretching group	Alkane, Aldehyde
2140-2100	C≡C Stretching group	Weak terminal alkynes
1725-1705	C=O Stretching group	Ester, Carboxylic acid, Ketone
1690-1600	C=N & C=C Stretching group, N-H Bending group	Oxime, monosubstituted conjugated alkene, cyclic alkene, amine

4.5. GC-MS Analysis

Table 3. GC-MS analysis of castor seed pyrolytic oil using Bentonite as Catalyst

Area%	Name of compound	Molecular formula
1.44	1-Nonene	C_9H_{18}
0.26	Cyclohexanecarboxylic acid, methyl ester	$C_8H_{12}O_3$
.81	4-Hexenoic acid	$C_6H_{12}O_2$
0.92	Phenol	C_6H_6O
1.29	1-Decene	C_9H_{20}
0.47	Decane	$C_{10}H_{22}$
0.29	2-Decene	C_9H_{20}
0.40	Phenol, 2-methyl	$C_7H_{10}O$
0.68	Benzene, (2-methylpropyl)	$C_{10}H_{14}$
1.89	p-Cresol	C_7H_8O
1.85	1-Undecene	$C_{11}H_{22}$
0.96	2-Methyllndene	$C_{10}H_{10}$
2.10	Dispiro[2.1.2.2]nonan-8-one	$C_9H_{12}O$
0.73	1-Dodecene	$C_{12}H_{24}$
0.44	Benzenepropanenitrile	$C_9H_{10}N_2O$
2.00	Benzene, hexyl	C_8H_{10}
1.04	Phenol, 2,6-dimethoxy	$C_8H_{10}O_3$
0.56	Benzene, heptyl	$C_{13}H_{20}$
2.41	Tropidine, 2-acetyl-8-demethyl-	$C_{10}H_{15}Cl_3$
0.60	4-Nonenal	$C_9H_{16}O$
0.38	10-Undecenoic acid, methyl ester	$C_{12}H_{22}O_2$
24.32	Undecylenic acid	$C_{11}H_{20}O_2$
0.53	2(1H)-Pyrimidinone	$C_4H_4N_2O$
4.22	Cyclopentadecane	$C_{15}H_{30}$
1.61	1,12-Tridecadiene	$C_{16}H_{29}$
4.86	Nonanamide	$C_{24}H_{52}N_8O_2$
1.92	E,E-9,11-Hexadecadien-1-ol	$C_{18}H_{32}O_2$
0.74	6,9-Heptadecadiene	$C_{17}H_{32}$

0.76	Dihydrofuranno(3,2-g)chroman	$C_6H_8O_3$
1.34	Benzenamine, 2,3,4,5,6-pentamethyl	$C_{11}H_{17}N$
0.32	1,5-Dodecadiene	$C_{12}H_{22}$
0.28	4-Phenylurazole	$C_8H_7N_3O_2$
0.33	Hexadecanenitrile	$C_{16}H_{31}N$
0.54	3,6-Dibutyl-1,2-dihydro-1,2,4,5-tetrazine	$C_{10}H_{20}N_4$
0.38	Tetradecanoic acid	$C_{14}H_{28}O_2$
1.05	Hexadecanenitrile	$C_{16}H_{31}N$
0.66	Pyrrolidine, 1-(6-hydroxy-1-oxooctadecyl)-	$C_{16}H_{13}NO$
3.91	Oleanitrile	C_4H_3N
1.42	Octadecanenitrile	$C_{18}H_{35}N$
1.10	Z,Z-8,10-Hexadecadien-1-ol	$C_{18}H_{32}O_2$
4.33	Indole, 2-methylamino-3-phenyl	$C_{15}H_{10}ClNO_2$
12.84	L-Proline, N-(5-fluoro-2-trifluoromethylbenzoyl)-, octadecyl ester	$C_9H_{16}ClF_3N_2$
1.38	1,11-Undecanediamine	$C_{11}H_{26}N_2$
1.13	2,11-Dodecadiene, 4-chloro	$C_{12}H_{21}Cl$
1.24	Desaspidinol	$C_{11}H_{14}O_4$
0.75	Isoelemicin	$C_{12}H_{26}O_3$
0.55	Isopropyl linoleate	$C_{21}H_{38}O_2$
2.97	Isopropyl linoleate	$C_{21}H_{38}O_2$
1.63	Methyl 9,12-heptadecadienoate	$C_{11}H_{22}O$
0.74	Methyl 5,11,14-eicosatrienoate	$C_9H_{19}O$
0.42	7-Deacetamidocolchicine	$C_{22}H_{25}NO_6$
0.20	1H-Indole, 5-methyl-2-phenyl	$C_{15}H_{13}N$

Table 4. GC-MS analysis of castor seed pyrolytic oil using Molecular Sieve as Catalyst

Area%	Name of compound	Molecular formula
1.46	1-Decene	C_9H_{20}
1.49	Cyclopentanone, 2-methyl	$C_6H_{10}O$
1.17	p-Cresol	C_7H_8O
1.47	5-Undecene	C11H22
2.19	7-Octenoic acid	$C_8H_{14}O_2$
1.18	Octanoic acid	$C_7H_{16}O_2$
1.06	Cyclodecane	$C_{10}H_{20}$
2.26	Nonanoic acid	$C_9H_{18}O_2$
1.35	n-Decanoic acid	$C_{10}H_{20}O_2$
3.38	Acephate	$C_4H_{10}NO_3PS$
35.60	Undecylenic acid	$C_{11}H_{20}O_2$
3.71	2-Nonenal, 2-pentyl	$C_{14}H_{26}O$
3.73	Dodecanamide	$C_{12}H_{25}NO$
3.12	8-Heptadecene	C17H34
2.24	cis,cis-7,10,-Hexadecadienal	$C_{18}H_{32}O_2$
1.06	1-Pentadecyne	C15H30
1.20	Tetradecanoic acid	$C_{14}H_{28}O_2$
3.74	Oleanitrile	C_4H_3N
1.53	Octadecanenitrile	$C_{18}H_{35}N$
8.45	4-Phenanthrenecarboxylic acid	$C_{85}H_{124}O_8$
14.79	1,3-Diaminonaphtho[2,3-f]quinazoline	$C_{12}H_{26}N_3O_2$
1.05	9,12-Octadecadienoic acid (Z,Z)-	$C_{18}H_{32}O_2$
0.80	2,4,7-Pteridinetriol, 6-ethyl- beta-Asarone	$C_{13}H_{28}O_3$
1.98	9-Octadecenamide, (Z)-	$C_{18}H_{35}NO$

Table 5. GC-MS analysis of castor seed pyrolytic oil using Zeolite as Catalyst

Area%	Name of compound	Molecular formula
0.88	1-Decene	C_9H_{20}
1.32	p-Cresol	C_7H_8O
0.87	Methylselenol	CH_4Se
0.97	Octanoic acid	$C_7H_{16}O_2$
0.66	Catechol	$C_6H_6O_2$
0.89	Nonanoic acid	$C_9H_{18}O_2$
2.01	Tricyclo[4.4.0.0(2,8)]decane	C_7H_7NO
0.50	10-Undecenoic acid, methyl ester	$C_{12}H_{22}O_2$
34.80	Undecylenic acid	$C_{11}H_{20}O_2$
2.56	2-Nonenal, 2-pentyl	$C_{14}H_{26}O$
1.99	Hexadecanamide	$C_{16}H_{33}NO$
0.36	1-Pentadecene	$C_{15}H_{30}$
0.47	8-Heptadecene	$C_{17}H_{34}$
0.17	Ricinoleic acid	$C_{18}H_{34}O_3$
1.47	n-Hexadecanoic acid	$C_{16}H_{32}O_2$
2.81	Oleanitrile	C_4H_3N
0.36	Methyl 9-cis,11-trans-octadecadienoate	$C_{19}H_{34}O_2$
0.88	1-Nonadecene	$C_{19}H_{38}$
8.16	9,12-Octadecadienoic acid (Z,Z)	$C_{18}H_{32}O_2$
8.74	Oleic Acid	$C_{18}H_{31}O_2$
2.16	Octadecanoic acid	$C_{18}H_{36}O_2$
2.58	10,12-Hexadecadien-1-ol	$C_{16}H_{30}O_2$
15.79	Pyrene, hexadecahydro	$C_{16}H_{26}$
4.12	2-Chloroethyl linoleate	$C_{20}H_{35}ClO_2$
0.40	Methyl 18-fluoro-octadec-9-enoate	$C_{23}H_{44}O_4$
0.60	9-Octadecenamide, (Z)-	$C_{18}H_{35}NO$
0.32	9-Octadecenamide, (Z)	$C_{18}H_{35}NO$

The bio-oil characterization was realized by using GC–Mass Spectrometry Table 2, 3, 4, shows the chemical composition of pyrolytic oil of catalytic pyrolysis using bentonite, molecular sieve and zeolite respectively. Areas of compounds in bio-oil are given in tables. It was found that the bentonite treated bio-oil consisted of around 54 compounds, molecular sieve treated bio oil consisted of 29 compounds and zeolite treated bio-oil consisted of 29 compounds. Taking into account of area percentage, the highest peak of total ion chromatogram (TIC) of compounds were Undecylenic acid, Pyrene, hexadecahydro, 1,3-Diaminonaphtho[2,3-f]quinazoline, L-Proline, N-(5-fluoro-2-trifluoromethylbenzoyl)-, octadecyl ester, Oleanitrile, Oleic Acid, 4-Phenanthrenecarboxylic acid, 9,12-Octadecadienoic acid (Z,Z), Indole, 2-methylamino-3-phenyl, Nonanamide, Dodecanamide, 2-Chloroethyl linoleate, Nonanamide, Isopropyl linoleate, Octadecanoic acid. Undecylenic acid is an organic unsaturated fatty acid. It is used in the manufacture of cosmetics and perfumery, pharmaceuticals, antimicrobial powders, including antidandruff shampoos and as a musk in perfumes and aromas. Undecylenic acid can be used in silicon-based biosensors. Oleic acid as its sodium salt is a major component of soap as an emulsifying agent. Small amounts of oleic acid are used as an excipient in pharmaceuticals. Oleic acid is used as an solubilizing agent in aerosol products. It is also used as emollient. Oleic acid is also used to induce lung damage in certain animals, for the purpose of testing new drugs and other means to treat lung diseases. As it can be observed the bio-oil contains compounds with carbon chain length in the range of C_4-C_{24} which is similar to most of fuels used.

4.6. Proximate Analysis of Pyrolytic Char

Table 6. Proximate Analysis of Pyrolytic Char

	Bentonite	Molecular Sieve	Zeolite
%Moisture	4.19	4.23	4.79
%Volatile Matter	15.92	15.82	15.92
%Ash	23.4	20.4	16.6
%Fixed Carbon	56.49	59.55	62.69

The Proximate analysis shows that the pyrolytic char contains maximum amount of fixed carbon of 62.69% at zeolite treated catalytic pyrolytic char.

4.7. SEM Analysis of Pyrolytic Char

The images of the char surface given by scanning electron microscope (SEM) at different magnification levels clearly shows reasonable amount of pores present on the surface.

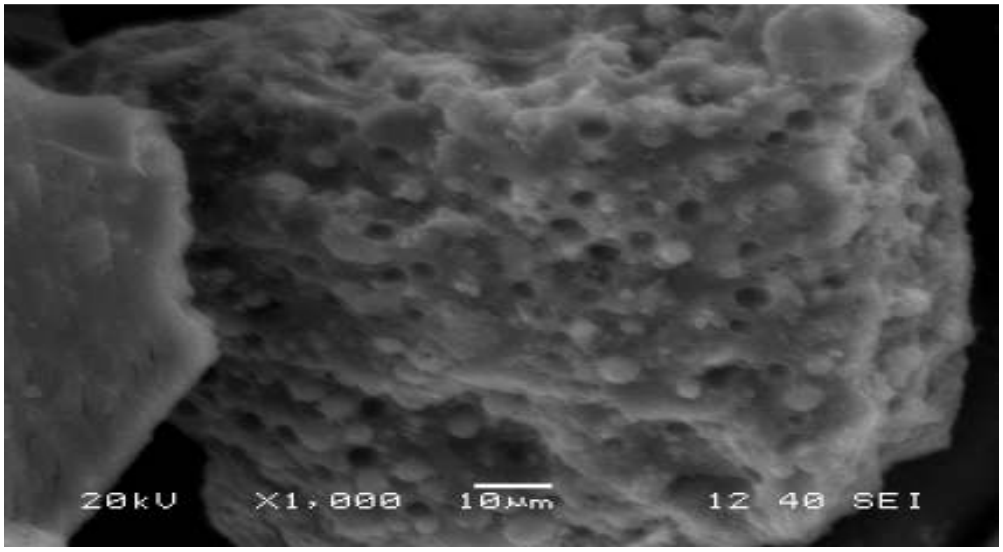

Fig. 16. SEM image of bentonite treated pyrolytic char.

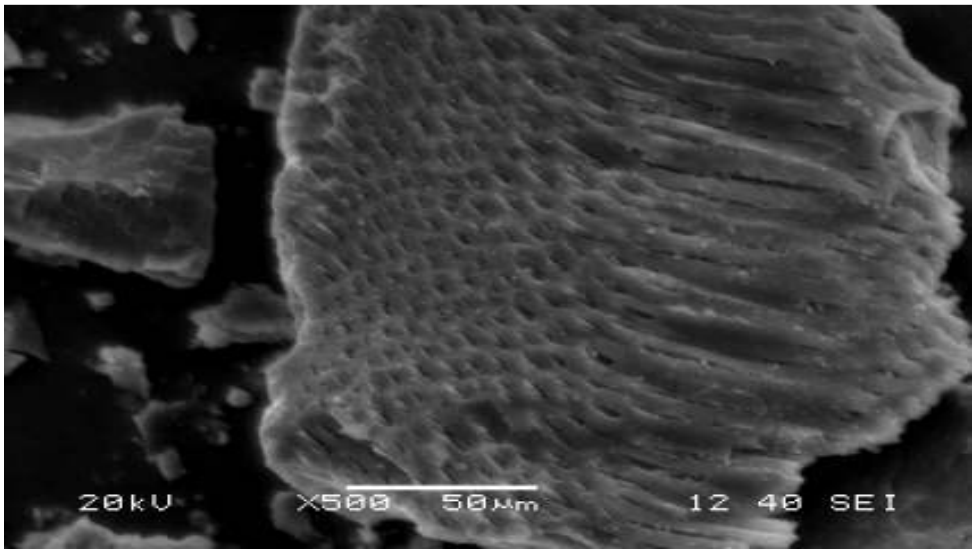

Fig. 17. SEM image of Molecular Sieve treated pyrolytic char.

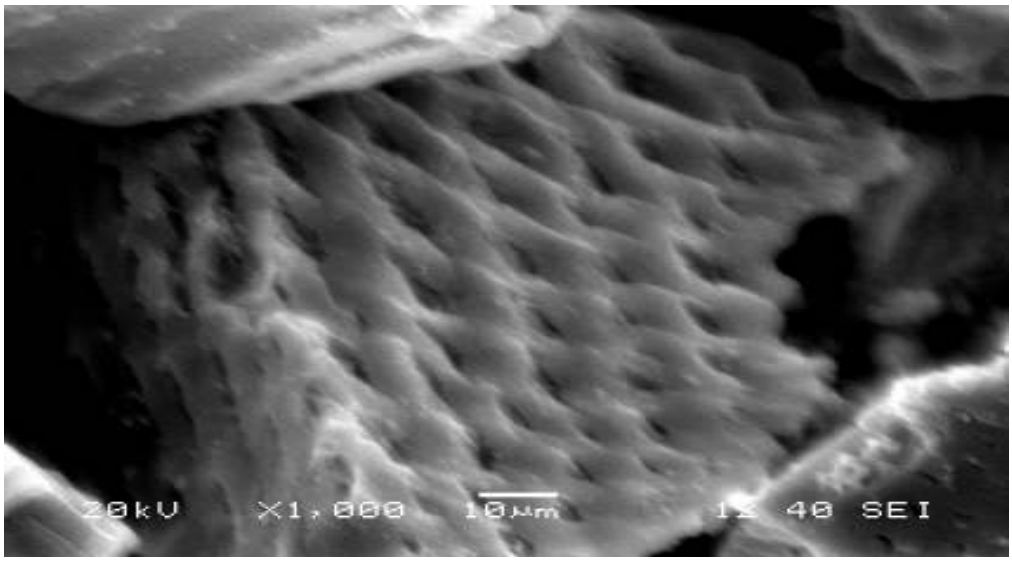

Fig. 18. SEM image of Zeolite treated pyrolytic char.

CONCLUSION

5. Conclusion

Catalytic pyrolysis of castor seeds was carried out in a semi batch reactor made up of stainless steel at temperature of 550^{o}C and at a rate of 20^{o}C/min to produce bio-fuel using Bentonite, Molecular Sieve and Zeolite as catalyst at the catalyst to biomass ratio ranging from 1:6 to 1:2. The maximum yield oil on wt. basis was obtained at the catalyst to biomass ratio of 1:5 for bentnoite, 1:4 for molecular sieve, and 1:5 for zeolite. Overall maximum yield of 62.73% was obtained in case of zeolite at the ratio of 1:5. As compared to the yield of thermal pyrolysis of castor seed without catalyst which was 64.4%, the yield of oil was significantly reduced after catalysis for the catalyzed reaction. The major compounds present in castor seed pyrolytic oil were Undecylenic acid, Pyrene, hexadecahydro; 1,3-Diaminonaphtho[2,3-f]quinazoline; L-Proline, N-(5-fluoro-2-trifluoromethylbenzoyl)-, octadecyl ester, Oleanitrile, Oleic Acid, 4-Phenanthrenecarboxylic acid, 9,12-Octadecadienoic acid (Z,Z), Indole, 2-methylamino-3-phenyl, Nonanamide, Dodecanamide, 2-Chloroethyl linoleate, Nonanamide, Isopropyl linoleate, Octadecanoic acid. It was observed that the bio-oil contains compounds with carbon chain length in the range of C_4-C_{24} which is similar to most of fuels used.

6. References:

1. World primary energy consumption by source, *Annual Energy Outlook 2013,* www.iea.org

2. http://www.mnre.gov.in, Ministry of new and renewable energy sources, govt. of india

3. P. Sudha, H.I. Somashekhar, Sandhya Rao, N.H. Ravindranath, "*Sustainable biomass production for energy in India*", Biomass and Bioenergy, Volume 25, Issue 5, November 2003, Pg. 501–515

4. India energy overview and analysis available, energy information administration(EIA), Official Energy Statistics from the U.S. Government, www.eia.gov

5. N.H. Ravindranath, C. Sita Lakshmi, Ritumbra Manuvie, P. Balachandra, "*Biofuel production and implications for land use, food production and environment in India*", Energy Policy, Volume 39, Issue 10, October 2011, Pg. 5737–5745

6. Ashwani Kumar, Kapil Kumar, Naresh Kaushik, Satyawati Sharma, Saroj Mishra, "*Renewable energy in India: Current status and future potentials*", Renewable and Sustainable Energy Reviews, Volume 14, Issue 8, October 2010, Pg. 2434–2442

7. Peter McKendry, "Energy production from biomass (part 2): conversion technologies", Bioresource Technology 83, 2002, Pg. 47–54

8. D.L. Klass, "*Biomass for renewable energy, fuels, and chemicals*", Academic Press, San Diego, CA, 1998

9. Serder Yaman, "*Pyrolysis of biomass to produce fuels and chemical feedstocks*", Energy Conversion and Management, 45, 2004, Pg. 651–671

10. French R., Czernik S. "*Catalytic pyrolysis of biomass for biofuels production",* Fuel Process Technology 91, 2010, Pg. 25–32

11. A. Aho, N. Kumar, K. Eranen, T. Salmi , M. Hupa, D. Yu. Murzin, "*Catalytic pyrolysis of woody biomass in a fluidized bed reactor: Influence of the zeolite structure",* Fuel 87, 2008, Pg. 2493–2501

12. Kaiqi Shi, Shuangxi Shao, Qiang Huang, Xuwen Liang, Lan Jiang, Ya Li, "*Review of Catalytic Pyrolysis of Biomass for Bio-oil*", Materials for Renewable Energy & Environment (ICMREE), 2011 International Conference on, Volume:1

13. Esben Taarning, Christian M. Osmundsen, ab Xiaobo Yang,a Bodil Voss,a Simon I. Andersena and Claus H. Christensena, "*Zeolite-catalyzed biomass conversion to fuels and chemicals*", Energy & Environmental Science, 2010

14. Pan Wang, Sihui Zhan , Hongbing Yu , Xufang Xue, Nan Hong, "*The effects of temperature and catalysts on the pyrolysis of industrial wastes (herb residue)*", Bioresource Technology 101, 2010, Pg. 3236–3241

15. Ilknur Demiral , Sevgi Sensoz, "*The effects of different catalysts on the pyrolysis of industrial wastes (olive and hazelnut bagasse)"*, Bioresource Technology 99, 2008 Pg. 8002–8007

16. Huiyan Zhang, Rui Xiao, He Huang, Gang Xiao, "*Comparison of non-catalytic and catalytic fast pyrolysis of corncob in a fluidized bed reactor*", Bioresource Technology 100, 2009, Pg. 1428–1434

17. Paul T. Williams, Nittaya Nugranad, "*Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks*", Energy 25, 2000, Pg. 493–513

18. Eleni Antonakou, Angelos Lappas, Merete H. Nilsen, Aud Bouzga, Michael Stocker, "*Evaluation of various types of Al-MCM-41 materials as catalystsin biomass pyrolysis for the production of bio-fuels and chemicals*", Fuel 85, 2006, Pg. 2202–2212

19. Suping Zhang , Yongjie Yan, Tingchen Li, Zhengwei Ren, "*Upgrading of liquid fuel from the pyrolysis of biomass*", Bioresource Technology 96, 2005, Pg. 545–550

20. Atte Aho, Narendra Kumar, Kari Eranen, Miko Hupa, Tapio Salmi, Dmitry Yu., Murzin, "*Zeolite-bentonite hybrid catalysts for the pyrolysis of woody biomass*", Studies in Surface Science and Catalysis Volume 174, Part B, 2008, Pg.1069–107

21. Egi Agustian, M. Ghozali, Savitri, Wuryaningsih SR, "*Biodiesel production of jatropha curcas oil by bentonite as catalyst*", Proceeding of International Conference on Sustainable Energy Engineering and Application, 18 July 2012

22. ASTM D 121 - *Standard Practice for Proximate Analysis of Coal and Coke*.

23. R.K. Singh, K.P. Shadangi, "*Liquid fuel from castor seeds by pyrolysis*", Fuel 90, 2011, Pg. 2538–2544